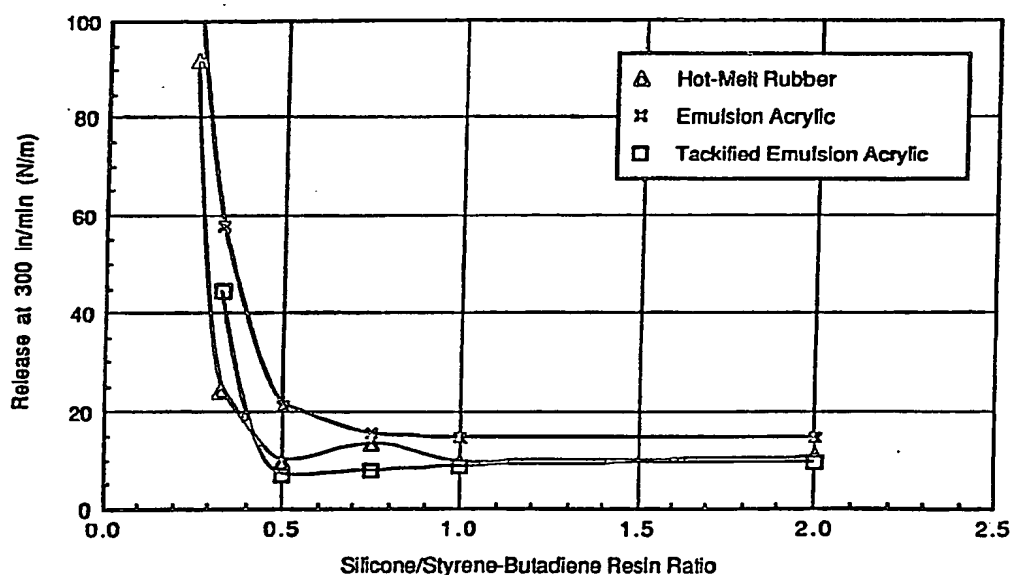




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(54) Title: IMPROVEMENTS RELATING TO ADHERENT SURFACES



(57) Abstract

A substrate is provided with a release surface by application of an emulsion of a vinyl-addition silicone system and catalyst therefor and a particulate component, preferably a resin. The vinyl addition silicone system is cured upon application of heat and removal of water.

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IMPROVEMENTS RELATING TO ADHERENT SURFACES

Background of the Invention

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This invention relates to release surfaces utile for release liners and adhesive contacting release surfaces for self-wound tapes among other applications.

20

A major utility of the invention concerns an improved release liner (or backing) for use in combination with a pressure-sensitive adhesive layer and a face stock preferably for label applications. In such combinations, the release liner protects the pressure-sensitive adhesive (PSA) prior to the label being used and is removed immediately prior to application of the label to another surface.

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Additionally, the release liner serves to facilitate cost effective manufacture of rolls or sheets of labels. It also functions as a carrier of labels for dispensing in automatic labeling operations and for computer printing in EDP applications. The performance attributes of a release liner are critical to both the manufacture and end-use application of pressure sensitive adhesive labels.

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In conventional practice, the release liner is provided as a silicone layer on a support layer having high holdout, i.e., the support layer on which the silicone layer is deposited is resistant to silicone penetration. Where the support layer is paper, a special and, therefore, expensive paper, such as a

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1 super-calendered or densified glossy paper, is required.
One currently accepted way of applying a silicone
release composition to a high-holdout support layer is
by solvent coating. Growing concern over the
5 environment has imposed stringent restrictions regarding
recovery of the solvent used in applying the solvent
based silicone to the high-holdout backing paper or
other materials.

An alternative to this is to use 100% solids
10 silicone release compositions. These are supplied with
a viscosity (usually <2000 cps) suitable for roll-
coating techniques. Application of these to porous
substrates such as low cost papers, machine finished
(MF) or machine glazed (MG) papers, finds these
15 materials to soak into the paper (penetrate the paper
surface) to give ineffective coverage of the paper
fibers unless excessively high quantities of expensive
silicone are used. Ineffective coverage of the paper
fibers provides unsuitable release liners for PSA
20 applications especially where high speed convertibility
is an essential performance feature.

A major application for a release liner is as part
of bulk rolls of laminate consisting of the release
liner, a face stock between which there is contained an
25 inherently tacky self-adhesive, or pressure-sensitive
adhesive. The adhesive may be permanent or
repositionable. The rolls are converted by printing
label information on the face stock, die cutting the
labels through the face stock and adhesive to the
30 surface of the release liner, followed by removal of the
matrix surrounding the labels thus leaving a plurality
of labels on the release liner.

It is important that the force required for release
be sufficiently low for the intended application, but
35 not so low that the die cut labels will release or
predispense from a moving web turning a corner or remove
with the waste matrix during its removal. The release

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1 force should also be not so high that the matrix is broken during its removal.

It would be desirable to provide a release liner which can be manufactured in a more economical fashion under a condition which eliminates the risk of environmental pollution, and in which the release level can be controlled at a variety of peel rates so as to enable high-speed convertibility, i.e., die cutting, matrix stripping.

10 Some attempts have been made to formulate release liners under environmentally safe conditions. U.S. Patents Nos. 4,618,657 and 4,713,410 to Katchko, et al., propose the application of a reactive silicone as a component of an aqueous emulsion which also contains a blend of a fluid hydroxyl-functional resin, which is a fatty acid, or fatty alcohol-containing polyester, and a crosslinking agent for the hydroxy resin. The silicone portion is either a hydroxy- or alkoxy-functional polysiloxane, or a vinyl-addition type silicone.

20 The hydroxyl-functional polysiloxanes are reactive with the hydroxyl-functionality in the polyol-modified polyester resin. Alkoxy-functionality is also reactive with hydroxyl-functionality in the polyester resin, and a tin-based catalyst assists these condensation reactions. The crosslinker (hydrogen-functional polysiloxane) of the vinyl-addition type silicone can also react with hydroxyl functionality of the polyester resin or with unsaturation in the polyester resin, as well as the vinyl portion of the vinyl-silicone base polymer.

30 The polyester resins described in the '657 patent are said to be of low molecular weight and are further defined in the '410 patent to be free flowing liquids at room temperature. As such, they too can permeate into porous surfaces such as low cost, MF or MG papers in a manner similar to the 100% solids silicones. Their primary utility lies in the use of less-expensive

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1 polyester resins with silicone emulsions to reduce the
overall cost of the release composition.

5 Among other difficulties with the systems described
in the '410 and the '657 patents is that stratification
must also occur, with the polyester resin stratifying to
the paper and the silicone stratifying or "blooming" to
the surface of the resin to form, in essence, a paper-
resin-silicone laminate. Stratification takes time, and
this results in liners having performance properties
10 which are dependent upon processing speed.

The technology of the '657 and '410 patents has
been evaluated, and the systems provided therein gave
backings exhibiting excessive resin penetration into the
machine-glazed paper backing and an appearance which
15 would preclude acceptance in the marketplace. After two
weeks at ambient temperature, these constructions
developed a strong, offensive odor. Release values,
when used in combination with a commercial emulsion
acrylic adhesive, were too high (i.e., 50 to 55 N/m) at
20 room temperature for all label applications. When the
silicone constituent was varied, release could be
lowered to 25 to 30 N/m at room temperature, but a
greater amount of silicone was required. Appearance
remained poor, with heavy streaking. Keil aging values
25 were not obtained.

U.S. Patent No. 4,362,833 to Mune, et al, describes
a system where a condensation-curable, hydroxyl-
functional emulsion silicone system is used in
combination with aqueous resins having film-forming
30 ability and bearing hydroxyl- and/or carboxyl-functional
groups. The silicone content is high, 50-80%. In
addition to having limited utility in respect to
emulsion acrylic adhesives, condensation-curable
silicones cure at an extremely slow rate, making them
35 commercially unattractive for high-speed web processes.

Similarly, Japanese Patent Publication Sho
51-139835 to Vemura describes an emulsion, contained

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1 therein in a reactive condensation curable silicone,
where the catalyst is an acid, alkali, amine, or organic
metal salt (usually tin salt) used in combination with a
resin emulsion. Where the resin may be inert, it is
5 preferably reactive with the silicone. This technology
would also be unsuitable for high-speed web processes.

 The present invention relates to the improvement in
the release surfaces utilizing aqueous-based silicone
resin systems not heretofore contemplated in the art and
10 adaptive to a broad-based utility in all phases where
release surface is required, including all applications
where controlled release is required.

Summary of the Invention

15 According to the present invention, there is
provided a release surface of controlled release force
for substrates including, but not limited to, release
liners suitable for use with pressure-sensitive
adhesives and other applications. Preferably, the liner
20 substrate is a paper and more preferably, a low-cost
porous paper. The substrate is furnished with a release
coating comprising a blend of a cured vinyl-addition
silicone component containing therein dispersed and
emulsifiable particles, and/or particle domains, as a
25 contained component, preferably domains of resin
particles. At silicone levels exceeding about 35% by
weight, the silicone exists as a continuous phase
surrounding the discrete particles and/or particle
domains. At lower silicone levels there is insufficient
30 silicone to surround all of the particles and the
resulting blend exhibits properties of both the silicone
and particle components. The coating is derived from an
aqueous-based emulsion, substantially free of organic
solvents. Release force or peel at a variety of peel-
35 rates is controlled by the silicone-to-particle ratio,
the nature of the particles used, the degree of
interaction between the silicone and particle phases,

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1 crosslinked density of the cured silicone phase, and
coat weight.

5 In the presently preferred embodiment, there is
provided a release liner comprising a porous paper
substrate, preferably a porous paper substrate such as
machine-glazed (MG) or machine-finished (MF) papers
furnished with a release surface comprising a polymer
blend of a cured vinyl-addition silicone component and
dispersed organic resin particles and/or domains. The
10 coating is derived from an aqueous-based emulsion of a
vinyl-addition silicone system, its catalyst and one or
more particle resins, essentially free of organic
solvents, the resin being essentially inert with respect
to the ability of the vinyl-addition silicone system to
15 undergo cure.

The silicone content of the coating can, depending
on the application, range from about 5 or less to about
80%, by weight, of the coating, preferably about 15 to
about 50% by weight, and more preferably, from about 20
20 to about 40% by weight.

The dispersed particulate component comprises the
balance of the coating and when a resin, may normally be
rubbers or synthetic polymers having a glass transition
temperature (Tg) from about -125° to greater than 100°C,
25 a number-average molecular weight greater than about 2
times its entanglement molecular weight (Me), and
typically having a particle size of about 2,500
Angstroms or less in the emulsion. Domains may have a
greater particle size.

30 The vinyl-addition silicone system is cured with a
Group VIII metal catalyst, with the preferred catalyst
being platinum in a complexed state. High rates of cure
are a feature of the invention.

35 In the production of the release surface of the
instant invention, the curable vinyl-addition silicone,
i.e., base vinyl unsaturated silicon polymer and
crosslinker silicone polymer and catalyst, the mutually

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1 combined emulsified particles or resin which must not
negatively influence the silicone curing reaction are
combined to achieve a mixture suitable for coating. To
5 achieve this result, the combined emulsion desirably has
a pH of less than about 8. Following coating, removal
of the water by drying (by application of heat and/or
air flow), and/or soaking into the porous paper, with
added heat, curing occurs. This provides a release
10 surface which is solid and remains substantially on the
surface of a substrate including porous paper. Bloom or
stratification is moot and negates the influence of
coating/curing rates on the performance of the liner.

Using this robust process of high speed cure of
compositions which do not require silicone separation
15 from other materials, or bloom or stratification into
discrete separate layers, products of substantially
identical quality can be produced at rates up to or
exceeding 3,000 feet per minute.

The products formed may be utilized in the full
20 range of release applications, especially
pressure-sensitive adhesive roll stock and converted at
high-speeds (die-cutting, matrix stripping) among other
applications. Release can be selectively tailored to
enable production of a laminate with tandem adhesive or
25 in off-line adhesive coating production modes without
sacrifice of excellent convertibility (i.e., die cutting
and matrix stripping), at reduced liner costs.

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1 Brief Description of the Drawings

FIG. 1 illustrates in block form the process used in the conduct of the invention;

FIGS. 2 and 3 illustrate matrix cutting apparatus;

5 FIG. 4 illustrates matrix removal from a converted roll label stock; and

FIG. 5 illustrates the release force required for matrix removal at 300 inches per minute as a function of silicone content for various pressure-sensitive
10 adhesives.

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1 Detailed Description

According to the present invention, there is provided novel, release surfaces enabling the production of low-cost release liners manufactured in an environmentally safe manner by emulsion coating of one or both sides of a liner substrate or web which may conveniently be a porous paper.

Features of the invention are that a coating applied as an emulsion using materials which gives good coating holdout on porous papers and enables high-speed cure, allowing a robust process, which gives the same type of product independent of whether coated and cured at the rate of 20 feet per minute or a rate of 3,000 feet per minute.

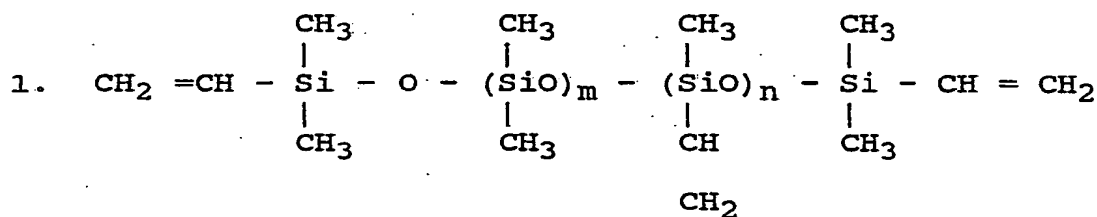
It also enables, over a broad range, the ability to adjust release to make the release effective with virtually any pressure-sensitive adhesive, and when formed into a laminate of release liner, pressure-sensitive adhesive and face stock, there is enabled excellent high-speed convertibility, i.e., die cutting and matrix stripping. A release surface made according to the present invention is made by coating a carrier such as a release liner paper stock, with aqueous emulsion of a curable vinyl-addition silicone system containing one or more vinyl unsaturated silicone polymers, one or more silicone hydride crosslinker, also a polymer, a Group VIII metal catalyst, preferably a platinum catalyst, and emulsified particles. The composition is free of ingredients which inhibit cure of the vinyl-addition silicone system. The coating is subjected to heat to drive off the water and initiate cure of the vinyl-addition silicone system, forming a blend on the paper in which the cured silicone phase contains therein substantially dispersed particle phases. The silicone phase may, depending on silicone concentration, be continuous or discontinuous. The particles may be individual or agglomerated, in whole or

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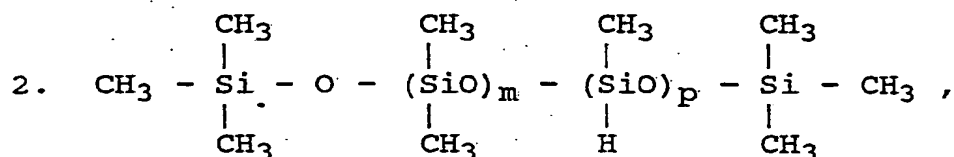
in part, to form domains, but are nevertheless still dispersed.

The silicone emulsions used in the present inventions are those which comprise silicone monomers having vinyl unsaturation which, when mixed with silicone hydride containing crosslinkers, is cured by a Group VIII metal catalyst, preferably a platinum catalyst. The emulsion, preferably contains reactive surfactants, that react with the silicone polymers so as not to interfere with pressure sensitive adhesive performance.

While not limiting presently preferred vinyl-addition silicone emulsions are mixtures of reactive vinyl silicone polymers of the formulas:



where m and n are independent integers, and silicone hydride crosslinking polymers of the formula;



where m and p are also independent integers.

There may also be included conventional ingredients designed to modify the release properties.

Vinyl-addition silicone systems react by thermally induced addition-cure (hydrosilation) between polydimethyl-hydrogen siloxane crosslinkers and reactive vinyl-functional silicone polymers to furnish a cured silicone release composition. Following cure, corona

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1 treatment may be employed to modify release properties.

The vinyl-functional silicone molecules are polydimethyl siloxanes, where some of the methyl groups have been substituted with vinyl groups or other alkyl groups containing vinyl unsaturation, i.e., the reaction takes place between a vinyl substituted polydimethyl siloxane and polydimethylhydrogen siloxane.

The whole hydrosilation is catalyzed by silicone soluble complex compounds of Group VIII transition metals, particularly platinum. In normal use of vinyl-addition silicone systems, a small amount of inhibitor is added to prevent premature reaction between the silicone hydride and vinyl silicone groups following mixing of the coating components, before deposition onto the substrate. This inhibitor is removed or made ineffectual during the thermal curing process. Suitable silicone emulsion systems for practice of this invention can be obtained from Dow Corning, Rhone-Poulenc and Wacker-Chemie GmbH, e.g., the Wacker VP 1571E/1572 System.

For further details, see "The Chemistry and Technology of Thermally Cured Silicone Release Agents," by Richard P. Eckberg, CONVERTING & PACKAGING, December 1987, pages 152 to 155, the contents of which article are incorporated herein by this reference.

The particles which form part of the silicone/particle emulsion for coating on the liner to form a release liner may be normally provided as an emulsion by the manufacturer, but also can be directly dispersed into a silicone emulsion or silicone added to a particle emulsion. The particles may be inorganic or organic in nature. Organic particle emulsion resins are preferred and include, among others, acrylate resins, ethylene-vinyl acetate copolymer resins, methacrylate resins, natural rubber, styrene polymers, styrene-acrylonitrile resins, olefin resins, styrene-butadiene resins (SBR), preferably carboxylated styrene-

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1 butadiene copolymers, styrene-isoprene and styrene-
butadiene random and block copolymers, chloroprene,
ethylene-vinyl acetate-acrylate terpolymers, silicone
5 polymers and the like. Resins typically have a glass
transition temperature (Tg) from about -125°C or less to
100°C or more, have a number average molecular weight
greater than about 2 times their entanglement molecular
weight (Me), and are of a particle size sufficiently low
10 to enable formation of an emulsifiable dispersion,
typically in the order of 2,500 Ångstroms or less.

The substrate or support (liner or web) to which
the emulsion is applied ("liner" herein) may be, but
need not be, a specialized, densified paper or other
material having silicone/solvent resistance (holdout).
15 For label application, a much less expensive paper is
preferred. When paper, the only characteristic required
of the paper is that it have a sufficient mechanical
strength, when both wet and dry, to be passed through
coating, converting, computer printing, and dispensing
20 operations without tear and have a caliper range to meet
final product and tooling specifications. Suitable
papers include MF and MG Kraft paper, super-calendared
or densified Kraft paper, vellum newsprint paper,
lightweight printing paper, and coated paper.
25 Mechanical and wood-free papers are permissible, as are
papers made from recycled fibers and the like. What is
unique and unexpected is that there may be substituted
30- to 40-pound per ream porous papers for 50-pound per
ream papers, which can be converted on the equipment
30 used with 50-pound per ream paper without equipment
modification. Other suitable substrates include porous
and nonporous plastics and fabrics, woven and non-woven,
for specialty applications.

Requirements of the mixed emulsion at the time of
35 application are that it has a suitable pH value and is
free of agents which inhibit cure or cure rate of the
vinyl-addition silicone system. Suitable pH is about 8

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1 or less, typically about 4 to about 7.0. Silicones are
supplied in emulsion with a solids content of normally
35 to 52%, while the resin emulsions are typically
5 supplied at a solids content of 35 to 70%. Depending
upon the paper and the design of the coating equipment,
the solids content of the net emulsion formed by mixing
the two may be modified to be as low as 5 to 10%, by
weight, and upwards of 25 to 65%, by weight, solids by
10 the use of additional water. Solids content may be
maximized to facilitate the coating, drying and curing
processes. Coating levels range from about 1 to about
10 grams/m², preferably about 2 to 5 grams/m² on a dry
basis.

15 The ratio of the resin-to-silicone can be varied,
and herein lies a particular benefit of the invention.
Surprisingly, by varying the ratio, the release level
can be varied easily and without recourse to control
release additives. At low release speeds (i.e.,
300"/min or less) the higher the ratio of resin to
20 silicone for a given coating, the higher the release
level. An acceptable weight ratio of resin-to-silicone,
can be from 19:1 to 1:4, i.e., (5 to 80%) with release
being controllable over a preferred silicone content of
about 15 to about 50% silicone, and for release liners
25 preferably about 20 to about 40% silicone. The use of
more than 40% silicone is usually unnecessary and
increases the cost of the coating without additional
performance benefit.

30 Without being bound by theory, the solids
(nonvolatile) content of the emulsions may be looked at
as paints, where the silicone emulsion is the vehicle
and the resin the pigment. The critical pigment volume
concentration (CPVC), as explained in "PAINT FLOW AND
35 "PIGMENT DISPERSION", John Wiley and Sons, Second
Edition, 1975, Chapter 5, incorporated herein by
reference, for monosize, spherical resin particles is
0.524 for loose packing and 0.724 with tight tetrahedral

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1 packing. In random packing, the value is 0.639. At the
CPVC, the spherical particles are just in contact with
each other and the silicone vehicle fills the voids
5 between the particles. Below the CPVC, or at higher
silicone levels, the particles lose contact with each
other by being separated by the silicone binder.
However, above the CPVC or higher resin level (>64%),
there is insufficient silicone to surround all the
10 particles. This results in coatings which provide
higher release values at low release speeds. At this
elevated resin level, if the resin has a $T_g > 5^\circ\text{C}$ the
overall modulus of the coating may be increased at
higher rates of peel, which may not lead to high energy
15 dissipation within the release coating, and high-speed
release values may be reduced.

If there is significant silicone surrounding the
particles (i.e., 50% silicone in the composition) or if
the particles are soft resins (resins with a $T_g < -20^\circ\text{C}$),
stresses on the surface at high rates of peel or release
20 may lead to dissipation of energy within this soft
polymer-blend network and provide increased release
levels with increasing rates of peel.

With reference now to FIG. 1, release liners of the
instant invention may be prepared according to the block
25 diagram shown therein. A liner, not shown, is coated
with a mixed silicone/particle emulsion. The liner may
be back-wetted with water, if desired, and passed to an
air flow oven, typically maintained at a temperature
above which the water will readily evaporate from the
30 emulsion, after which the catalyst will cause cure of
the silicone resin to form a silicone phase in which
there is dispersed particles. Because the silicone
paper is now dry, it may be remoisturized with water to
prevent curl. This provides an effective release liner
35 which can be sold as such for coating with a hot melt,
emulsion, or solvent adhesive. Time to cure with high
air flow ovens is as short as 1.2 seconds, enabling

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1 machine speeds of up to 3,000 feet per minute, and also
permits another unique feature of the invention, tandem
coating with the adhesives. The exceptional feature of
the release liners of the invention is that, even with
5 the use of low-cost and lighter weight papers, e.g., 30-
to 40-pound per ream paper, label constructions
utilizing the release liners of the invention are
especially adapted to conventional die cutting and
matrix stripping at high conversion rates on equipment
10 designed for higher paper weights, e.g., 40 or 50
pounds. The conversion process is illustrated in FIGS.
2, 3, and 4.

With reference thereto, matrix-stripped label stock
is conventionally converted from a pressure-sensitive
15 adhesive label stock 10, comprised of a face material
12, a pressure-sensitive adhesive layer 14, and a
release liner 16, being passed between driven-anvil roll
18 and driven-die roll 20, having cutting edges 22, with
penetration of the die into the laminate being
20 determined by breaker 24. Labels 26 are cut to the
release liner. There is removed from the laminate a
matrix web 28 which, as illustrated in FIG. 4, bears the
outline of the labels cut. The cut matrix web, which is
waste, is wound for disposal.

25 Examples of presses used for the die cutting and
the matrix stripping include the Webtron 650, which has
an operating speed of up to 650 feet per minute, and the
Mark Andy 4120 press, which processes stock up to 15-1/2
inches wide, and has an operating speed of up to 1,000
30 feet per minute.

Compositions of the instant invention may be varied
in release properties taking into consideration the
adhesive used to achieve not only adhesive coating rates
at the highest rates of adhesive coating applications,
35 but also achieve conversion by die cutting and matrix
stripping as described above at rates exceeding those
experienced with conventional 100% solids silicones on

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1 SCK (super-calendered Kraft) backings.

2 In particular, constructions containing the release
3 liner of this invention have demonstrated superior
4 converting performance as against traditional super
5 calendered kraft (SCK) liner containing constructions.
6 In wide web converting (i.e., 15-1/2" web width)
7 converting trials of a hot melt adhesive containing
8 construction with liners of this invention, converting
9 speeds of approximately 650 to 775 feet per minute were
10 realized using a standard four-up label die. The final
11 converted product displayed excellent layflat
12 characteristics. In contrast, the conventional SCK
13 liner constructions displayed maximum converting speeds
14 of but 450 to 500 feet per minute.

15 FIG. 5 shows the release characteristics as a
16 function of styrene-butadiene resin (particulate
17 component) to silicone ratio for three different
18 pressure-sensitive adhesives.

19 While a primary application of the invention is for
20 single or double coated release liners, other
21 applications include: embossing strip release liners,
22 protective release surfaces for floor tiles and wall
23 coatings, release papers for low pressure plastic
24 laminates, release materials for interleaves, release
25 materials for self-sealing roofing, bakery tray liners,
26 and like applications where a release surface of some
27 definite release value exists.

28 The invention is further illustrated by the
29 following nonlimiting Examples and Controls.

30

Example I

31 This Example illustrates the preparation of a
32 release liner using a porous MG Kraft paper by applying
33 a mixture of emulsion silicone polymers and an emulsion
34 resin. Such a paper substrate is unsuited to
35 conventional siliconizing as practiced in the pressure-
sensitive laminate manufacturing industry.

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1 The Example also illustrates that, by changing the
ratio of resin to silicone in the release coating, the
ease of separation of a self-adhesive laminate product
from such a liner can be controlled.

5 To make the emulsion release coating, the emulsion
silicone polymers were VP 1571E/1572, commercially
available from Wacker Chemie, mixed with the resin
emulsion known as Baystal P1800 from Bayer, with ratios
10 of 4:1 and 7:3 (dry weight resin: dry weight silicone).
No special equipment or precautions are needed. Water
may be added, if desired, to facilitate coating the
substrate paper with the mixture.

15 The mixture was Meyer-rod-coated onto sheets of a
commercially available MG Kraft paper using a laboratory
pilot coater. The coated sheets were then placed in an
oven at 130°C for 20 seconds to dry the emulsions and
cure the silicone layer.

20 The sheets were removed from the oven and coated
with an emulsion acrylate pressure-sensitive adhesive.
After drying the adhesive, a face stock (label paper)
was applied to the adhesive layer.

 Throughout the whole experiment conditions were
kept constant to eliminate erroneous results due to
variations in manufacturing conditions.

25 Release force is the force required to peel a strip
of face stock of given dimensions from the release
liner, or vice versa. The method used in these
instances was the FINAT release test, i.e., the force
required to peel a one-inch (2.54 cm) wide strip of
30 release liner from its face stock. The results obtained
are given below in Table 1.

Table 1

	Ratio Rubber:Silicone	Release Force (N/m)
35	4:1	22.8
	7:3	13.9

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1 Example II

 In this Example, the ratios of resin to silicone ratios were varied and the adhesive was changed to a hot melt, i.e., an adhesive made from synthetic thermoplastic block copolymers blended with tackifiers and oils. Hot melt adhesive is applied as a hot, melted plastic which, when cool, acts as a pressure-sensitive adhesive. The method of manufacture is essentially the same as in Example 1, but the adhesive is applied by an extrusion die at the desired coating weight.

 Throughout the whole experiment conditions were kept constant to eliminate erroneous results due to variations in manufacturing conditions.

15 Table 2

	Ratio Rubber:Silicone	Release Force (N/m)
	1:2	5.4
	4:3	7.7
	2:1	10.4
20	3:1	23.2

 The above Examples clearly show that simply by varying the ratio of rubber to silicone, the release levels can be easily varied for a given adhesive.

25

Example III

 Although the observed change in properties of the release coating of this invention at silicone to non-silicone ratios about the CPVC (36% silicone as the fluid phase and 64% non-silicone resins as the dispersed phase), implies that the release coating achieved by practice of this invention is a composition wherein at silicone levels exceed 36% by weight the cured silicone phase surrounds a substantially discrete particulate phase or domains, additional efforts were undertaken to characterize these coatings. One purpose of this effort was to obtain confirmation that the unique combinations

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1 of materials described in this patent application
provide release compositions that are unknown to the
prior art which describe achievement of release
properties with mixed systems via silicone bloom or
5 stratification.

A Wacker 1571E/1572 emulsion silicone was mixed
together with Polysar 3083 emulsion containing a
styrene-butadiene copolymer resin at a ratio of one part
silicone per two parts SB resin on a solids basis. This
10 was coated onto a machine glazed kraft paper using roll-
coating methods. This was passed through a high-airflow
oven at elevated temperature to remove the water and
cure the silicone phase. Following remoisturization, a
suitable release liner was obtained, a portion of which
15 was used for characterization as described below.

A Transmission Electron Microscope (TEM) was used
to study thin cross sections of the liner which had been
subjected to osmium tetroxide staining.

The osmium tetroxide adds to unsaturation in
20 organic compositions to provide darker areas to the TEM
where such unsaturation exists. The SB copolymer in the
release coating of this example contains unsaturation.

The TEM pictures showed dark domains among a white
background. The size of some of these domains were
25 substantially the same as the SB resin particles (1350Å)
in the original SB resin emulsion as determined by light
scattering techniques. The domains as a whole were
dispersed and did not form a separate layer.

Additional confirmation for this description was
30 obtained by making thick (1/16") pieces of the coating
(Wacker 1571E/1572 with Polysar 3083 SB resin) at a
variety of silicone to resin ratios (100 to 0%). This
was done by slow evaporation of the water phase of the
mixtures in a Teflon mold. This was followed by cure of
35 the silicone at elevated temperatures to obtain pieces
which were evaluated for their visco-elastic properties
using a Rheometrics RMS-800 Mechanical Spectrometer.

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1 The data obtained confirms that at silicone levels
exceeding 30% the silicone is predominately the
continuous phase with the SB copolymer resin as a
particulate, dispersed phase. At lower levels of
5 silicone there is a formation of a polymer blend having
both silicone and SB copolymer resin domains. Evidence
for the interaction between these phases was also noted.

Differential Scanning Calorimetry (DSC) data on
these thick pieces of coating composition supports the
10 above description, including the interaction between the
silicone and the SB resin phases.

Example IV

Mixtures of silicone emulsion Wacker 1571E/1572 and
15 Polysar 3083 styrene-butadiene emulsion resin were made
at six different silicone-to-resin ratios (solids
basis). These were Meyer-rod-coated onto a 32-pound
per ream machine finished paper from James River-Otis,
dried and cured in a high air flow oven to produce
20 release liners suitable for use with pressure-sensitive
adhesives. These were coated with three different
adhesives (a rubber/resin as a hot melt, an emulsion
acrylic, and an emulsion tackified acrylic) and
laminated with a facestock (following drying of the
25 emulsion adhesives) to produce constructions for release
testing after 24 hours of aging. The data for this
testing is presented graphically in Figure 5.

It is apparent that papers of low basis weight can
function as release liners when used with compositions
30 of this invention and that they are suitable for use
with several types of pressure sensitive adhesives.
Additionally, it is shown that control of release level
may be achieved by varying the ratio of silicone to
resin in the coating composition.

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Example V

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Mixtures of Wacker silicone emulsion 1571E/1572 and Bayer P5900 styrene-butadiene resin emulsion were made at three different silicone to resin ratios (25, 33, 50% silicone). These were coated onto a machine glazed Kraft paper by roll coating techniques on a production-type coater, dried and cured in a high air flow oven to produce release liners suitable for use with pressure sensitive adhesives. These release liners were then coated with a tackified acrylic emulsion adhesive, dried and laminated with a face stock and provided a functional pressure-sensitive adhesive stock useful for die cutting and matrix stripping to form labels at high speeds.

Examples VI to XI

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To determine the utility of additional types of resin emulsions as a mixture with vinyl silicone emulsion systems, several different commercial resin emulsions were mixed with the Wacker 1571E/1572 silicone emulsion being used at three silicone to resin ratios (20, 35, 50% silicone on a solids basis). These were Meyer rod coated onto a machine glazed Kraft paper, dried and cured in a high air flow oven to produce release liners for testing.

30

To these liners there were laminated two tapes having either a solvent-based rubber/resin adhesive or a solvent-based metal crosslinked acrylic adhesive. Both of these adhesives are known to be aggressive to release compositions. The resulting constructions were subjected to 24-hour room temperature aging and Keil aging, then tested for release level at 300"/min peel and loop tack properties.

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Keil aging is a form of accelerated aging (70°C, 1/4 PSI, 20 hours) and is viewed as providing a worst-case of what might be obtained with extended room temperature aging.

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1 Loop tack testing has been found to be very
discriminating in demonstrating transfer of materials
from the release composition to applied adhesives.
Reduction in tack properties is not necessarily
5 indicative of loss of adhesive properties unless it is
extreme (retention of <25% tack properties).

 The resins for this evaluation comprise commercial
materials having Tgs as high as 103°C and as low as
-60°C. The two resins having Tgs of 100 and 103°C would
10 not be considered film forming materials and thus
further distinguish this invention from some art which
calls for good film formers as the nonsilicone portion
of the coating compositions.

 Additionally, it is of interest to note that the
15 acrylate polymer of Avery Chemical is a commercial
pressure-sensitive adhesive.

 The data for evaluation of the utility of these
additional resin emulsions is presented in Table 3.

 It is apparent that many types of resin emulsions
20 have utility with the present invention. Seemingly, the
only restriction is that the resulting mixtures provide
composition suitable for coating, and that the resin
emulsion not inhibit the cure or cure rate of the
silicone emulsion.

 It is also shown that the resulting polymer blends
25 from these mixtures also provide higher release values
at concentrations exceeding the CPVC (as discussed
above) or less than 36% silicone. Additionally, it is
seen that the release level can also be controlled by
30 choice of the resin phase in these poly-blend release
coatings. Thus, both the amount and the type of resin
phase can be used to control the release level of
compositions of this invention. It is shown that the
degree of adhesive interaction with compositions of this
35 invention are dependent on the type of adhesive used
(release level is different for the rubber/resin
adhesive as compared to the acrylic adhesive) and thus

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1 compositions for release coatings of this invention can
be chosen to maximize the performance of the
constructions having different adhesives.

5 Although there is some reduction in loop tack
properties of adhesives with liners of these examples in
comparison to the control release liner which has a
well-cured 100% solids silicone release composition on a
super-calendered Kraft paper, this loss is not deemed
excessive and yet will provide constructions suitable
10 for a wide range of products. The loss is considered to
be primarily from the surfactants in the silicone and
the resin emulsions (the greater the resin
concentration, the greater the tack loss) and is a
consideration when selecting a resin emulsion from
15 supplier.

20

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30

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Table 3

Example MANUFACTURER PRODUCT COMPOSITION T _g (°C)	VI		VII		VIII		IX		X		XI	
	BF Goodrich HYCAR - 2600X374 MMA 103		Morton Thiokol Iytron 621 Modified - Polystyrene 100		DuPont Neoprene Latex 115 Neoprene -36		Avery Chemical AE 220HS/H Emulsion Acrylic Adhesive -51		BF Goodrich Hystretch - Latex V-60 Acrylic -60		GE GE 5000 100% Silicone - Coating -120	
I. RELEASE (g/2in)[90°, 300ipm]												
RUBBER/RESIN SOLVENT ADHESIVE												
20% SILICONE	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL
35% SILICONE	17.6	979.0	13.0	457.4	16.1	224.8	39.9	227.4	77.2	255.9		
50% SILICONE	18.1	190.6	4.1	185.4	22.3	199.9	5.2	175.1	43.0	129.0		
100% SILICONE	23.8	82.4	5.2	69.4	24.9	131.1	5.2	140.9	35.2	115.0	5.2	18.1
METAL-CROSSLINKED ACRYLIC SOLVENT ADHESIVE												
20% SILICONE	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL
35% SILICONE	81.3	481.7	44.0	407.1	53.4	137.3	15.5	207.7	148.7	240.9		
50% SILICONE	35.2	97.4	26.4	111.4	54.9	115.5	11.9	146.6	84.4	123.8		
100% SILICONE	68.4	60.1	16.6	58.2	46.1	88.6	6.7	72.0	50.2	76.7	8.8	15.0
II. LOOP TACK (N/M)												
RUBBER/RESIN SOLVENT ADHESIVE												
20% SILICONE	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL
35% SILICONE	1187	581	1175	1115	1062	871	1339	709	853	556		
50% SILICONE	1463	1151	1346	1161	1119	1002	1273	650	807	617		
100% SILICONE	1502	1295	1522	1522	1093	1094	1418	801	932	787	1625	1523
METAL-CROSSLINKED ACRYLIC SOLVENT ADHESIVE												
20% SILICONE	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL	RT	KEIL
35% SILICONE	497	476	463	380	410	403	383	417	311	447		
50% SILICONE	506	556	483	414	341	422	417	418	446	384		
100% SILICONE	568	576	420	466	344	475	399	451	476	516	588	600

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Example XII

To further demonstrate the ability to control the release profile (release level vs. release speed) by choice of the resin and the concentration of the resin phase in the silicone phase of the polymer-blend release coatings of this invention, the following compositions were made at two ratios of silicone to resin (33 and 20% silicone) and tested for release level at two peel speeds (300 "/min and 1200"/min).

The emulsions Wacker silicone 1571E/1572 were mixed with Polysar 3083 styrene-butadiene resin ($T_g = 25^\circ\text{C}$), Flexcryl 1653 ethylene-vinylacetate-acrylate resin from Air Products and Chemicals ($T_g = -32^\circ\text{C}$), or Nicoseal 3-2160 poly-2-ethylhexylacrylate resin from IGI Adhesives ($T_g = -60^\circ\text{C}$). These were Meyer-bar-coated onto a machine-glazed paper and put into a high airflow oven for removal of the water and cure of the silicone phase to produce liners for testing. To these were laminated a tape having a hot melt rubber/resin adhesive to make constructions for testing following 24 hours of aging at room temperature. The result of this testing is provided in Table 4.

Table 4

<u>Resin</u>	<u>% Silicone</u>	Release @	Release @
		300 in/min <u>(N/m)</u>	1200 in/min <u>(N/m)</u>
3083	33	6.8	8.4
	20	7.1	6.4
1653	33	9.9	40.5
	20	23.8	40.5
3-2160	33	14.7	64.9
	20	125.0	126

It is apparent that control of the release profile (release level vs. release speed) can be achieved by choice of the type and amount of resin phase of release coatings of this invention.

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Examples XIII to XVII and Controls A to C

The following study was performed to establish the flexibility of using release liners of the instant invention in the conversion process of FIGS. 2, 3 and 4. Normally a converter has little flexibility in the weight (lbs./ream) of the liner which can be processed with a particular equipment set-up. In accordance with the invention, low weight papers can be used on systems set for papers of higher weight. What will be considered are conversion equipment used for 40- and 50-pound per ream release liner paper, where again the die cuts to the release liner, to show that lower weight papers can be used provided there is employed the release compositions of the invention. In particular, there was in each instance a release liner having as the release surface the composition 33% by weight silicone with a Polysar 3083 styrene-butadiene resin of Examples 4 and 12. The paper weight in pounds per ream and its manufacturer are shown in Tables 5, 6 and 7 and compared to the standard release paper as the control. Table 8 shows the die configurations used. In the tables, the face material 12 was a 50-pound per ream high gloss (Table 5), 50- pound per ream electronic data processing paper (Table 6) and Vellum (Table 7). The pressure-sensitive adhesive was a commercial hot melt adhesive based on a tackified Kraton styrene-isoprene-styrene block copolymer. In determining release values, the release liner is pulled from the face stock (liner off) or the face stock and adhesive pulled from the liner (face off). In evaluating the various runs, the "run speed" means the speed at which the operator felt waste was minimal; "hangers" gives a speed range over which one or more die cut labels will remain with the matrix, while "flags" means the range over which matrix breakage can occur for the die cut matrices of Table 8.

The results clearly establish that using release liners of the invention paper weight can be readily

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- 1 varied without modifying equipment and good conversion achieved.

Table 5

5

Liner	Ex. XIII 30# Flexpac	Ex. XIV 32# MF J.R. Dunn	Control A 40# SCK(a)
-------	----------------------------	--------------------------------	-------------------------

Release Values (N/m):

10	Liner Off	19/20	3/7	9/12
	Face Off	16/22	9/12	13/15

Webtron Converting Details (Meters/min.):

15	Die #1	Run Speed	70	200	200
		Hangers	30-200	None	None
		Flags	85-200	None	None
20	Die #2	Run Speed	120	200	200
		Hangers	130-134	None	None
		Flags	130-134	None	None
25	Die #3	Run Speed	76	200	200
		Hangers	46-200	None	None
		Flags	84-200	None	None
30	Die #8	Run Speed	145	200	200
		Hangers	46-200	None	None
		Flags	183-200	None	None

(a) Super-calendared Kraft

30

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Table 6

5

Liner	Ex. XV 40# MG- J.R. Dunn	Ex. XVI 35# MG- Geo. Pacific	Ex. XVII 40# MG- Thil.	Control B 50# SCK(a)
-------	--------------------------------	------------------------------------	------------------------------	-------------------------

Release Values (N/m):

Liner Off	13/16	24/27	19/23	26/28
Face Off	23/23	24/30	21/28	28/24

10

Webtron Converting Results (Meters/min.):

15

Die #1	Run Speed	200	200	200	200
	Hangers	None	None	None	None
	Flags	None	None	None	None
Die #3	Run Speed	200	200	200	200
	Hangers	None	None	None	None
	Flags	None	None	None	None
Die #8	Run Speed	200	200	200	200
	Hangers	None	None	None	None
	Flags	None	None	None	None

20

(a) Super-calendared Kraft

Table 7

25

Liner	Ex. XVIII 40# MG- Thil.	Ex. XIX 40# MG- Thil.	Control C 50# SCK(a)
-------	-------------------------------	-----------------------------	-------------------------

Mark Andy Converting Details (Meters/min.):

30

Die C*	Run Speed	100	100	100
	Flags	107-110	75-110	76-110
	Hangers	107-110	107-110	107-110

(*Includes in-line fanfolding)

35

Die A	Run Speed	183	236	139
	Flags	183-261	198-253	145-244
	Hangers	244-261	244-253	152-244

(a) Super-calendared Kraft

Table 8

Die Descriptions

<u>Die</u>	<u>Label Size (WXL)</u>	<u>Web Width</u>	<u>Number Across Web</u>	<u>Number Around Web</u>	<u>Cross Direction Matrix</u>	<u>Machine Direction Matrix</u>	<u>Label Corner Radius</u>
#1	4-1/2 x 15/16 in.	5 in.	1	6	1/16 in.	---	1/8 in.
#2	1-7/8 x 2-25/32 in.	6-1/2 in.	3	2	1/8 in.	1/8 in.	1/16 in.
#3	5 x 3 in.	5-1/2 in.	1	2	1/16 in.	---	1/16 in.
#8	3 x 2-1/16 in.	6-1/2 in.	2	2	3/32 in.	1/8 in.	3/16 in.
A	3-1/2 x 2-15/16 in.	14-3/4 in.	4	---	1/16 in.	1/10 in.	---
C	5 x 2-7/8 in.	11 in.	2	---	1/8 in.	1/8 in.	---

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1 What Is Claimed Is:

5 1. A release liner suitable for use with pressure-sensitive adhesives which comprises a liner substrate having a release coating comprising a blend of a cured silicone polymer component and a particulate component, the cured silicone polymer component being derived from a vinyl-addition silicone system comprised of at least one vinyl silicone polymer, at least one
10 silicone hydride crosslinker catalyzed by a Group VIII metal catalyst, the coating being derived from an aqueous-based emulsion of a curable vinyl-addition silicone system and particulate component.

15 2. A release liner suitable for use with pressure-sensitive adhesives comprising a substrate having a release coating comprising a polymeric blend of a cured silicone component and a particulate resin component, the cured silicone component being derived
20 from vinyl-addition silicone system comprised of at least one vinyl silicone polymer and at least one silicone hydride crosslinker catalyzed with a Group VIII catalyst, the particulate resin component comprising at least one resin and the coating being derived from
25 aqueous-based emulsion containing both a vinyl-addition silicone system and a particulate resin component.

30 3. A release liner as claimed in claim 1, in which the cured silicone resin component is present in an amount of from about 5 to about 80 percent by weight based on the weight of the cured silicone component and particulate component.

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1 4. A release liner as claimed in claim 1 in which
the cured silicone resin component is present in an
amount of from about 15 to about 50 percent by weight
based on the weight of the cured silicone component and
5 particulate component.

 5. A release liner as claimed in claim 1, wherein
the cured silicone resin component is present in an
amount of from about 20 to about 40 percent by weight
10 based on the weight of the cured silicone component and
particulate component.

 6. A release liner as claimed in claim 1, wherein
the liner is paper.
15

 7. A release liner according to claim 6, wherein
the paper stock is a porous paper.

 8. A release liner as claimed in claim 7, wherein
20 the paper stock is selected from Kraft paper, vellum
newsprint stock, coated papers, wood-free papers, and
papers made from recycled fiber.

 9. A release liner as claimed in claim 7 in which
25 the paper is machine finished or machined glazed paper.

 10. A release liner as claimed in claim 1 in which
the Group VIII metal is platinum.

30 11. A release liner as claimed in claim 2, in
which cured silicone resin is present in an amount of
from about 5 to about 80 percent by weight based on the
weight of the cured silicone component and particulate
resin component.

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1 12. A release liner as claimed in claim 2 in which
the cured silicone resin is present in an amount of from
about 15 to about 50 percent by weight based on the
weight of the cured silicone component and particulate
5 resin component.

 13. A release liner as claimed in claim 2, wherein
the cured silicone component is present in an amount of
from about 20 to about 40 percent by weight based on the
10 weight of the silicone component and the particulate
resin component.

 14. A release liner as claimed in claim 2, wherein
the liner is paper.
15

 15. A release liner according to claim 14, wherein
the paper is porous paper.

 16. A release liner as claimed in claim 15,
20 wherein the paper stock is selected from Kraft paper,
super-calendared Kraft paper, vellum newsprint stock,
coated papers, wood-free papers, and papers made from
recycled fiber.

 17. A release liner as claimed in claim 15 in
25 which the paper is machine finished or machine glazed
paper.

 18. A release liner as claimed in claim 2 in which
30 the Group VIII metal is platinum.

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1 19. A release liner suitable for use with
pressure-sensitive adhesives comprises a porous paper
substrate having a release coating comprising a polymer
blend of a cured silicone component and a particulate
5 resin component, the cured silicone component being
derived from vinyl-addition silicone system comprising
at least one vinyl silicone polymer and at least one
silicone hydride crosslinker catalyzed with a platinum
catalyst, in which there is dispersed the particulate
10 resin component, the resin component comprising resins
having a glass transition temperature of from about
-125°C to about 100°C, a number average molecular weight
greater than 2 times its entanglement molecular weight
and being essentially inert to the cure of the
15 vinyl-addition silicone system, and the coating being
derived from aqueous-based emulsion of the
vinyl-addition silicone system and the particulate resin
component.

20 20. A release liner as claimed in claim 19 in
which the cured silicon resin component is present in an
amount of from about 5 to about 80 percent by weight
based on the weight of the cured silicone component and
the particulate resin component.

25 21. A release liner as claimed in claim 19 in
which the cured silicone resin component is present in
an amount of from about 15 to about 50 percent by weight
based on the weight of the cured silicone component and
30 particulate resin component.

35 22. A release liner as claimed in claim 19 wherein
the cured silicone resin component is present in an
amount of from about 20 to about 40 percent by weight
based on the weight of the cured silicone component and
resin component.

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1 23. A release liner as claimed in claim 19 wherein
the porous paper is selected from Kraft paper, vellum
newsprint stock, coated papers, wood-free papers, and
papers made from recycled fiber.

5 24. A release liner as claimed in claim 19 in
which the paper is machine finished or machine glazed
paper.

10 25. A release liner as claimed in claim 19 in
which the resin component is selected from the group
consisting of acrylic resins, ethylene-vinyl acetate
resins, methacrylate resins, natural rubber, styrene
resins, styrene acrylonitrile resins, styrene-butadiene
15 resins, styrene isoprene resins, chloroprene, and
mixtures thereof.

20 26. A release liner as claimed in claim 2 in which
the resin component is selected from the group
consisting of acrylic resins, ethylene-vinyl acetate
resins, methacrylate resins, natural rubber, styrene
resins, styrene-acrylonitrile resins, styrene-butadiene
resins, styrene-isoprene resins, chloroprene, and
mixtures thereof.

25 27. A substrate providing a release surface in
which such release surface comprises a coating which is
a blend of a cured silicone polymer component containing
a particulate component, the cured silicone polymer
component being derived from a vinyl-addition silicone
30 system comprised of at least one vinyl silicone polymer,
at lease one silicone hydride crosslinker catalyzed by a
Group VIII metal catalyst, said release surface being
derived from an aqueous-based emulsion of a curable
35 vinyl-addition silicone system and particulate
component.

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1 28. A substrate providing a release surface in
which such release surface comprising a coating which is
a polymeric blend of a cured silicone component and a
particulate resin component, the cured silicone
5 component being derived from vinyl-addition silicone
system comprised of at least one vinyl silicone polymer
and at least one silicone hydride crosslinker catalyzed
with a Group VIII catalyst, the particulate resin
component comprising at least one resin said release
10 surface being derived from aqueous-based emulsion of the
vinyl-addition silicone system and the particulate resin
component.

15 29. A substrate as claimed in claim 27 in which
the cured silicone resin component is present in an
amount of from about 5 to about 80 percent by weight
based on the weight of the cured silicone component and
particulate component.

20 30. A substrate as claimed in claim 27 in which
the cured silicone resin component is present in an
amount of from about 15 to about 50 percent by weight
based on the weight of the cured silicone component and
particulate component.

25 31. A substrate as claimed in claim 27 wherein the
cured silicone resin component is present in an amount
of from about 20 to about 40 percent by weight based on
the weight of the cured silicone component and
30 particulate component.

32. A substrate as claimed in claim 27 wherein the
liner is porous paper.

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1 33. A substrate as claimed in claim 32 wherein the
paper stock is selected from Kraft paper, vellum
newsprint stock, coated papers, wood-free papers, and
papers made from recycled fiber.

5 34. A substrate as claimed in claim 27 in which
the Group VIII metal is platinum.

10 35. A substrate as claimed in claim 28 in which
cured silicone resin is present in an amount of from
about 5 to about 80 percent by weight based on the
weight of the cured silicone component and particulate
resin component.

15 36. A substrate as claimed in claim 28 in which
the cured silicone resin is present in an amount of from
about 15 to about 50 percent by weight based on the
weight of the cured silicone component and particulate
resin component.

20 37. A substrate as claimed in claim 28 wherein the
cured silicone component is present in an amount of from
about 20 to about 40 percent by weight based on the
weight of the silicone component and the particulate
25 resin component.

 38. A substrate as claimed in claim 28 wherein the
liner is porous paper.

30 39. A substrate as claimed in claim 38 wherein the
paper stock is selected from Kraft paper,
super-calendared Kraft paper, vellum newsprint stock,
coated papers, wood-free papers, and papers made from
recycled fiber.

35 40. A release liner as claimed in claim 28 in
which the Group VIII metal is platinum.

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1 41. A substrate providing a release surface in
which the release surface comprises a coating of a
polymer blend of a cured silicone component and a
particulate resin component, the cured silicone
5 component being derived from vinyl-addition silicone
system comprising at least one vinyl silicone polymer
and at least one silicone hydride crosslinker catalyzed
with a platinum catalyst, in which there is dispersed
the particulate resin component, the resin component
10 comprising resins having a glass transition temperature
of from about -125°C to 100°C , a number average
molecular weight greater than 2 times its entanglement
molecular weight, and being essentially inert to the
cure of the vinyl-addition silicone system, said release
15 surface being derived from aqueous-based emulsion of the
vinyl-addition silicone system and the particle resin
component.

20 42. A substrate as claimed in claim 41 in which
the cured silicon resin component is present in an
amount of from about 5 to about 80 percent by weight
based on the weight of the cured silicone component and
the particulate resin component.

25 43. A substrate as claimed in claim 41 in which
the cured silicone resin component is present in an
amount of from about 15 to about 50 percent by weight
based on the weight of the cured silicone component and
particulate resin component.

30 44. A substrate as claimed in claim 41 wherein the
cured silicone resin component is present in an amount
of from about 20 to about 40 percent by weight based on
the weight of the cured silicone component and resin
35 component.

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1 45. A substrate as claimed in claim 41 in which
the resin component is selected from the group
consisting of acrylic resins, ethylene-vinyl acetate
resins, methacrylate resins, natural rubber, styrene
5 resins, styrene-acrylonitrile resins, styrene-butadiene
resins, styrene-isoprene resins, chloroprene, and
mixtures thereof.

10 46. A substrate as claimed in claim 28 in which
the resin component is selected from the group
consisting of acrylic resins, ethylene-vinyl acetate
resins, methacrylate resins, natural rubber, styrene
resins, styrene-acrylonitrile resins, styrene-butadiene
resins, styrene-isoprene resins, chloroprene, and
15 mixtures thereof.

20 47. A pressure-sensitive adhesive stock suitable
for label formation by converting which comprises a
laminate, a face stock, a pressure-sensitive adhesive
layer and a release liner in which the release liner
provides a release coating comprising a blend of a
cured silicone polymer component containing a
particulate component, the cured silicone polymer
component being derived from a vinyl-addition silicone
25 system comprised of at least one vinyl silicone polymer,
at least one silicone hydride crosslinker catalyzed by a
Group VIII metal catalyst, the coating being derived
from an aqueous-based emulsion of a curable
vinyl-addition silicone system and particulate
30 component.

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1 48. A pressure-sensitive adhesive stock suitable
for label formation by conversion which comprises a face
stock, a pressure-sensitive adhesive layer and a release
5 liner in which the release liner provides a release
coating comprising a polymeric blend of a cured silicone
component and a particulate resin component, the cured
silicone component being derived from vinyl-addition
10 silicone system comprised of at least one vinyl silicone
polymer and at least one silicone hydride crosslinker
catalyzed with a Group VIII catalyst, the particulate
resin component comprising at least one resin and the
coating being derived from aqueous-based emulsion of the
vinyl-addition silicone system and the particulate resin
component.

15 49. A pressure-sensitive adhesive stock as claimed
in claim 47 in which the cured silicone resin component
is present in an amount of from about 5 to about 80
percent by weight based on the weight of the cured
20 silicone component and particulate component.

 50. A pressure-sensitive adhesive stock as claimed
in claim 47 in which the cured silicone resin component
is present in an amount of from about 15 to about 50
25 percent by weight based on the weight of the cured
silicone component and particulate component.

 51. A pressure-sensitive adhesive stock as claimed
in claim 47 wherein the cured silicone resin component
30 is present in an amount of from about 20 to about 40
percent by weight based on the weight of the cured
silicone component and particulate component.

 52. A pressure-sensitive adhesive stock as claimed
35 in claim 47 wherein the liner is paper.

 53. A pressure-sensitive adhesive stock as claimed

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1 in claim 52 wherein the paper stock is a porous paper.

5 54. A pressure-sensitive adhesive stock as claimed in claim 52 in which the paper is a less than 50-pound per ream paper.

10 55. A pressure-sensitive adhesive stock as claimed in claim 52 in which the paper is a 40-pound per ream paper.

56. A pressure-sensitive stock as claimed in claim 53 in which the paper is about a 30-pound per ream paper.

15 57. A pressure-sensitive adhesive stock as claimed in claim 56 wherein the paper stock is selected from Kraft paper, super-calendared Kraft paper, vellum newsprint stock, coated papers, wood-free papers, and papers made from recycled fiber.

20 58. A pressure-sensitive adhesive stock as claimed in claim 56 in which the paper is machine finished or machined-glazed paper.

25 59. A pressure-sensitive adhesive stock as claimed in claim 47 in which the Group VIII metal is platinum.

30 60. A pressure-sensitive adhesive stock as claimed in claim 48 in which cured silicone resin is present in an amount of from about 5 to about 80 percent by weight based on the weight of the cured silicone component and particulate resin component.

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1 61. A pressure-sensitive adhesive stock as claimed
in claim 48 in which the cured silicone resin is present
in an amount of from about 15 to about 50 percent by
weight based on the weight of the cured silicone
5 component and particulate resin component.

 62. A pressure-sensitive adhesive stock as claimed
in claim 48 wherein the cured silicone component is
present in an amount of from about 20 to about 40
10 percent by weight based on the weight of the silicone
component and the particulate resin component.

 63. A pressure-sensitive adhesive stock as claimed
in claim 48 wherein the liner is paper.

15 64. A pressure-sensitive adhesive stock as claimed
in claim 63 wherein the paper is porous paper.

 65. A pressure-sensitive adhesive stock as claimed
20 in claim 63 in which the paper is less than about a
50-pound per ream paper.

 66. A pressure-sensitive adhesive stock as claimed
in claim 63 in which the paper is about a 40-pound per
25 ream paper.

 67. A pressure-sensitive stock as claimed in claim
64 in which the paper is a 30-pound per ream paper.

30 68. A pressure-sensitive adhesive stock as claimed
in claim 67 wherein the paper stock is selected from
Kraft paper, super-calendared Kraft paper, vellum
newsprint stock, coated papers, wood-free papers, and
papers made from recycled fiber.

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1 69. A pressure-sensitive adhesive stock as claimed
in claim 68 in which the paper is machine finished or
machine glazed paper.

5 70. A pressure-sensitive adhesive stock as claimed
in claim 48 in which the Group VIII metal is platinum.

10 71. A pressure-sensitive adhesive stock suitable
for conversion to labels which comprises a laminate of a
face stock contacting the pressure-sensitive adhesive
and pressure-sensitive adhesive layer and a release
liner formed of a porous paper substrate having a
release coating comprising a polymer blend of a cured
15 silicone component and a particulate resin component,
the cured silicone being derived from vinyl addition
silicone system comprising at least one vinyl silicone
polymer and at least one silicone hydride crosslinker
catalyzed with a platinum catalyst, in which there is
dispersed the particulate resin component, the resin
20 component comprising at least one resin having a glass
transition temperature of from about -125°C to about
100°C, a number average molecular weight greater than 2
times its entanglement molecular weight, and being
essentially inert to the cure of the vinyl-addition
25 silicone system, said coating being derived from
aqueous-based emulsions of the vinyl-addition silicone
system and the particle resin components.

30 72. A pressure-sensitive adhesive stock as claimed
in claim 71 in which the cured silicon resin component
is present in an amount of from about 5 to about 80
percent by weight based on the weight of the cured
silicone component and the particulate resin component.

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1 73. A pressure-sensitive adhesive stock as claimed
in claim 71 in which the cured silicone resin component
is present in an amount of from about 15 to about 50
percent by weight based on the weight of the cured
5 silicone component and particulate resin component.

 74. A pressure-sensitive adhesive stock as claimed
in claim 71 wherein the cured silicone resin component
is present in an amount of from about 20 to about 40
10 percent by weight based on the weight of the cured
silicone component and resin component.

 75. A pressure-sensitive adhesive stock as claimed
in claim 71 wherein the porous paper is selected from
15 Kraft paper, super-calendared Kraft paper, vellum
newsprint stock, coated papers, wood-free papers, and
papers made from recycled fiber.

 76. A pressure-sensitive adhesive stock as claimed
20 in claim 71 in which the paper is machine finished or
machine glazed paper.

 77. A pressure-sensitive adhesive stock as claimed
in claim 71 in which porous paper is less than about a
25 50-pound per ream paper.

 78. A pressure-sensitive adhesive stock as claimed
in claim 72 in which the porous paper is about a 30-
pound per ream paper.

30 79. A pressure-sensitive adhesive stock as claimed
in claim 71 in which the resin component is selected
from the group consisting of acrylic resins, ethylene-
vinyl acetate resins, methacrylate resins, natural
35 rubber, styrene resins, styrene acrylonitrile resins,
styrene-butadiene resins, styrene-isoprene resins,
chloroprene, and mixtures thereof.

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1 80. A pressure-sensitive adhesive stock as claimed
in claim 48 in which the resin component is selected
from the group consisting of acrylic resins, ethylene-
vinyl acetate resins, methacrylate resins, natural
5 rubber, styrene resins, styrene-acrylonitrile resins,
styrene-butadiene resins, styrene-isoprene resins,
chloroprene, and mixtures thereof.

10 81. A thermally-curable aqueous emulsion
comprising:

water;

at least one surfactant;

at least one emulsifiable particulate
component; and

15 a curable vinyl-addition silicone system
comprised of at least one vinyl silicone polymer, at
least one silicone hydride crosslinker and a Group VIII
metal catalyst, said emulsion having a pH of less than
about 8 and being substantially free of ingredients
20 which inhibit cure of the vinyl addition silicone
system.

 82. A thermally-curable aqueous emulsion
comprising:

25 water;

at least one surfactant;

at least one emulsifiable particulate resin
component and a vinyl-addition silicone system comprised
of at least one vinyl silicone polymer and at least one
30 silicone hydride crosslinker catalyzed with a Group VIII
metal catalyst, said emulsion having a pH less than
about 8 and being substantially free of ingredients
which inhibit cure of the vinyl addition silicone
system.

35 83. An emulsion as claimed in claim 81 in which
the pH is from about 4 to about 7.

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1 84. An emulsion as claimed in claim 82 in which
the pH is from about 4 to about 7.

5 85. An emulsion as claimed in claim 80, in which
the cured silicone resin component is present in an
amount of from about 5 to about 80 percent by weight
based on the weight of the cured silicone component and
particulate component.

10 86. An emulsion as claimed in claim 81 in which
the curable vinyl-addition silicone resin system is
present in an amount of from about 15 to about 50
percent by weight based on the weight of the vinyl-
addition silicone system and particulate component.

15 87. An emulsion as claimed in claim 81, wherein
the curable vinyl-addition silicone resin system is
present in an amount of from about 20 to about 40
percent by weight based on the weight of the vinyl-
20 addition silicone system and particulate component.

 88. An emulsion as claimed in claim 81 in which
the paper is machine finished or machined glazed paper.

25 89. An emulsion as claimed in claim 81 in which
the Group VIII metal is platinum.

30 90. An emulsion as claimed in claim 82, in which
curable vinyl-addition silicone system is present in an
amount of from about 5 to about 80 percent by weight
based on the weight of the vinyl-addition silicone
system and particulate resin component.

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1 91. An emulsion as claimed in claim 82 in which
the curable vinyl-addition silicone system is present in
an amount of from about 15 to about 50 percent by weight
based on the weight of the vinyl-addition silicone
5 system and particulate resin component.

 92. An emulsion as claimed in claim 82, wherein
the curable vinyl-addition silicone system is present in
an amount of from about 20 to about 40 percent by weight
10 based on the weight of the vinyl-addition silicone
system and the particulate resin component.

 93. An emulsion as claimed in claim 82 in which
the Group VIII metal is platinum.
15

 94. A thermally curable emulsion comprising:
 water;
 at least one surfactant; and
 an emulsified blend of resin components and a
20 vinyl-addition silicone system comprising at least one
vinyl silicone polymer and at least one silicone hydride
crosslinker catalyzed with a platinum catalyst, in which
the resin component comprising at least one resin having
a glass transition temperature of from about -125°C to
25 about 100°C, a number average molecular weight greater
than 2 times its entanglement molecular weight, and
being essentially inert to the cure of the
vinyl-addition silicone system.

30 95. An emulsion as claimed in claim 81 in which
the surfactant is a reactive surfactant.

 96. An emulsion as claimed in claim 82 in which
the surfactant is a reactive surfactant.
35

 97. An emulsion as claimed in claim 94 in which
the surfactant is a reactive surfactant.

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98. An emulsion as claimed in claim 94 in which the curable vinyl-addition silicon resin component is present in an amount of from about 5 to about 80 percent by weight based on the weight of the vinyl-addition silicone resin component and the particulate resin component.

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10

99. An emulsion as claimed in claim 94 in which the curable vinyl-addition silicone resin component is present in an amount of from about 15 to about 50 percent by weight based on the weight of the vinyl-addition silicone resin component and particulate resin component.

15

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100. An emulsion as claimed in claim 94 wherein the silicone resin component is present in an amount of from about 20 to about 40 percent by weight based on the weight of the vinyl-addition silicone resin component and resin component.

25

101. An emulsion as claimed in claim 82 in which the resin component is selected from the group consisting of acrylic resins, ethylene-vinyl acetate resins, methacrylate resins, natural rubber, styrene resins, styrene-acrylonitrile resins, styrene-butadiene resins, styrene-isoprene resins, chloroprene, and mixtures thereof.

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102. An emulsion as claimed in claim 94 in which the resin component is selected from the group consisting of acrylic resins, ethylene-vinyl acetate resins, methacrylate resins, natural rubber, styrene resins, styrene-acrylonitrile resins, styrene-butadiene resins, styrene-isoprene resins, chloroprene, and mixtures thereof.

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1 103. A method for forming a release liner which comprises applying to a porous paper substrate:

 (a) a thermally-curable aqueous emulsion comprising:

5 water;

 at least one surfactant;

 at least one emulsifiable particulate resin component comprising at least one resin having a glass transition temperature of from about -125°C to about
10 100°C, and a number average molecular weight greater than 2 times its entanglement molecular weight, and a vinyl-addition silicone system comprised of at least one vinyl silicone polymer and at least one silicone hydride crosslinker catalyzed with a platinum catalyst, said
15 emulsion having a pH less than about 8 and being substantially free of ingredients which inhibit cure of the vinyl addition silicone system; and

 (b) heating the emulsion coated paper to eliminate water and cure the vinyl-addition silicone
20 system to provide a polymer blend of resin particles and cured vinyl-addition silicone.

 104. A method as claimed in claim 103 in which there is thereafter applied to the cured vinyl-
25 addition silicone system of the release liner a layer of a pressure sensitive adhesive and a face stock.

 105. A method as claimed in claim 104 in which indicia is printed on the face stock and labels formed
30 by matrix cutting the face stock to the release liner to form said labels and a surrounding matrix followed by stripping the matrix from the release liner.

 106. A method as claimed in claim 104 in which the
35 pH is from about 4 to about 7.

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1 107. A method as claimed in claim 106 in which
the curable vinyl-addition silicone resin system is
present in an amount of from about 15 to about 50
percent by weight based on the weight of the vinyl-
5 addition silicone system and particulate component.

 108. A method as claimed in claim 106 in which the
paper is about 30-pound per ream machine finished or
machined glazed paper.

10 109. A release liner suitable for use with
pressure-sensitive adhesives which comprise a machine
glazed or machine finished porous paper substrate of a
weight from about 30 to 40 pounds per ream having a
15 release coating thereon comprising a cured silicone
component and a resin component, the cured silicone
component being derived from a vinyl-addition silicone
system comprising at least one vinyl silicone polymer
and at least one silicone hydride crosslinker catalyzed
20 with a platinum catalyst, the resin component comprising
at least one resin having a glass transition temperature
of from about -125°C to about 100°C, and a number
average molecular weight greater than 2 times the
entanglement molecular weight, and being essentially
25 inert to the cure of the vinyl-addition silicone system,
the coating being derived from an aqueous-based emulsion
of the vinyl-addition silicone system and the resin
component in particulate form.

30 110. A release liner as claimed in claim 109 which
the cured silicone resin component is present in an
amount of from about 20 to about 40 percent by weight
based on the weight of the cured silicone component and
resin component.

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1 111. A release liner as claimed in claim 109 in
which the resin component is selected from the group
consisting of acrylic resins, ethylene-vinyl acetate
resins, methacrylate resins, natural rubber, styrene
5 resins, styrene acrylonitrile resins, styrene butadiene
resins, styrene isoprene resins, chloroprene, and
mixtures thereof.

10 112. A release liner as claimed in claim 110 in
which the resin component is selected from the group
consisting of acrylic resins, ethylene-vinyl acetate
resins, methacrylate resins, natural rubber, styrene
resins, styrene acrylonitrile resins, styrene butadiene
resins, styrene isoprene resins, chloroprene, and
15 mixtures thereof.

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Fig. 1

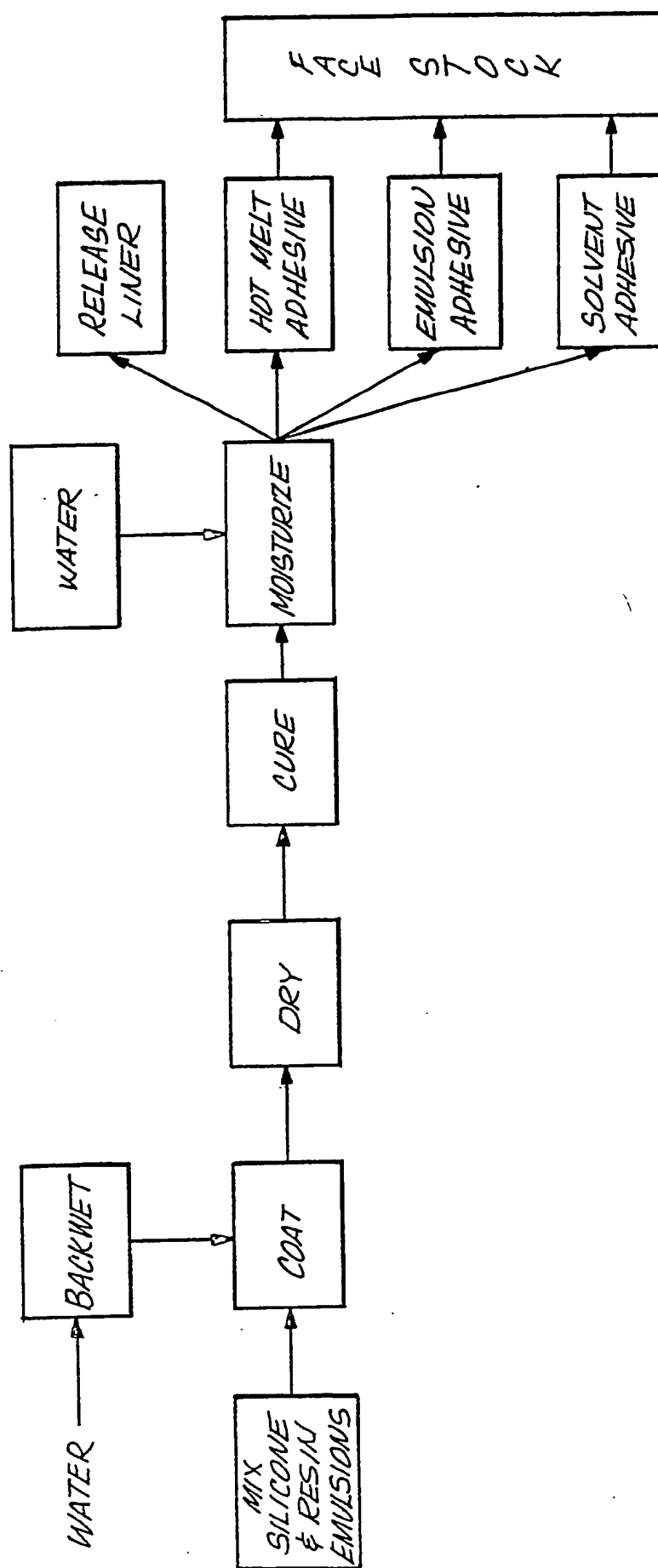


Fig. 2.

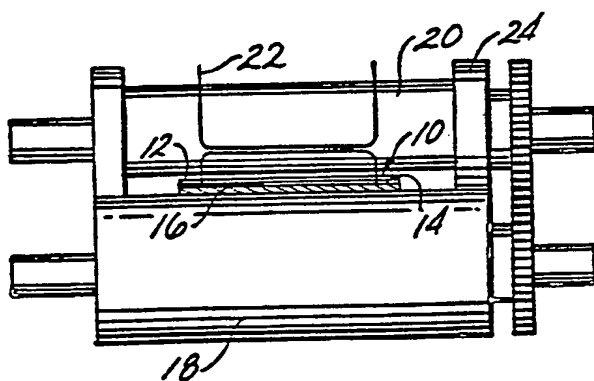


Fig. 3.

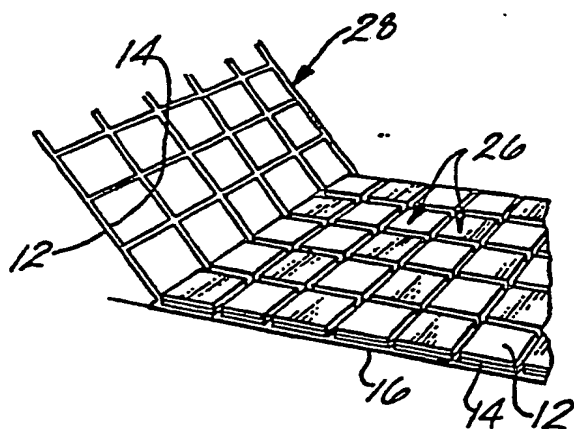
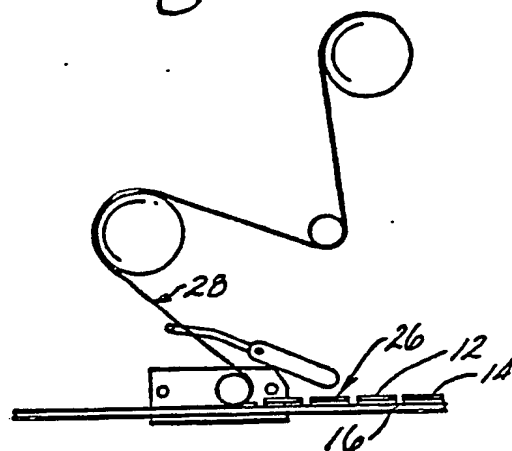
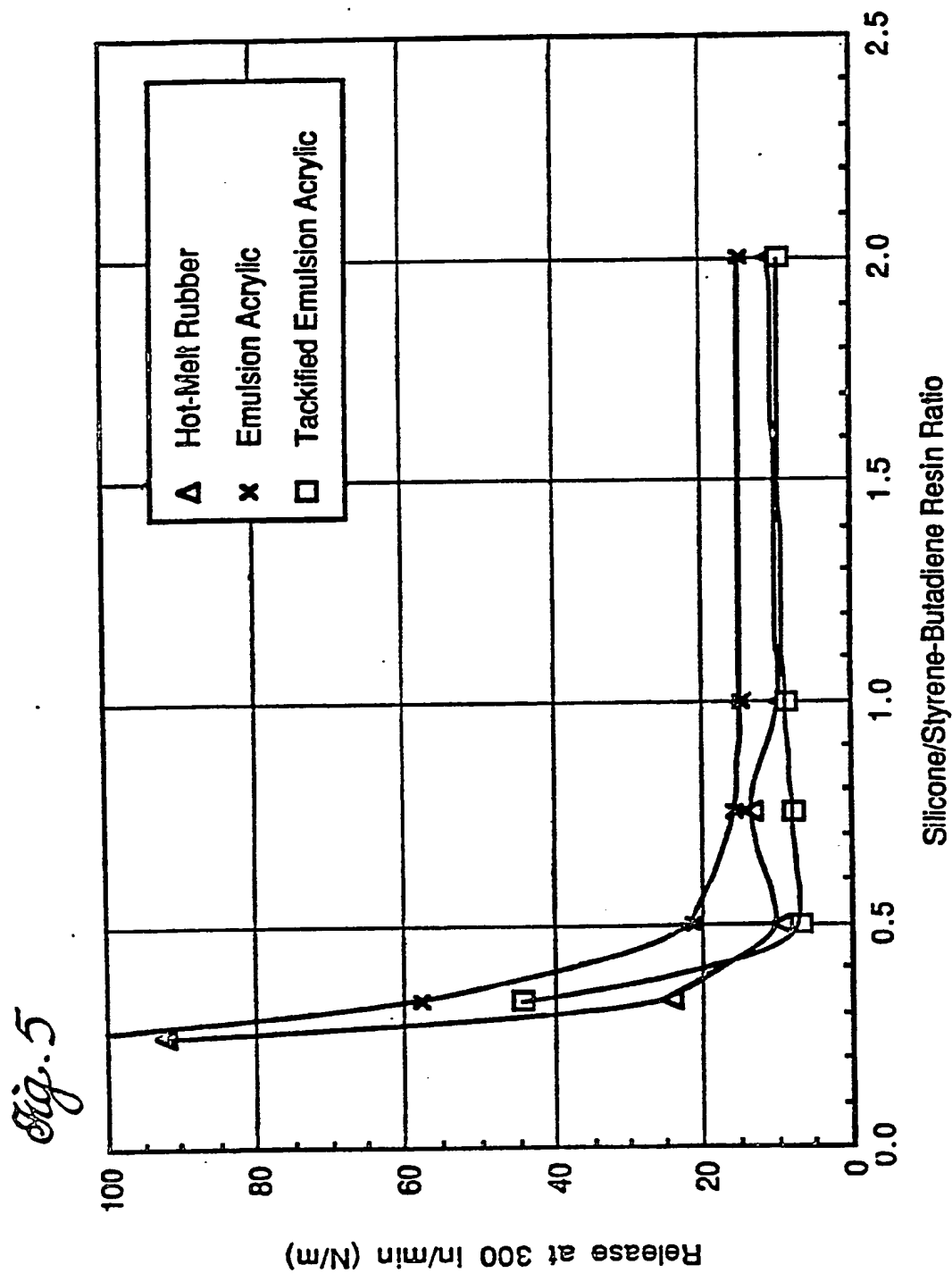


Fig. 4.



INTERNATIONAL SEARCH REPORT

International Application

PCT/US89/02/42

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): B32B 5/16, 25/14, 29/06

U.S. CL. 428/327, 352, 452

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
U.S.	428/327, 352, 452, 40, 449, 354; 427/387; 528/15; 525/478

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 3,328,482 (Northrup) 27 June 1967	1-18, 27-40 47-70, 81-93
Y	US, A, 3,933,702 (Caimi) 20 January 1976 See entire document especially column 6, lines 16-23, column 3, lines 7, 8 and column 13, lines 36-38.	1-24, 27-44, 47-78, 81-94 97-100, 103-110
Y	US, A, 4,624,900 (Fau) 25 November 1986	all claims
Y	US, A, 4,533,575 (Melancon) 6 August 1985 See entire document, especially column 7, lines 48-56.	1-18, 27-40, 47-70, 81-96 103, 109
A	US, A, 4,190,688 (Traver) 26 February 1980	1-112
Y	US, A, 4,618,657 (Katchko) 21 October 1986 See entire document, especially column 3, lines 17-55.	1-112
Y	US, A, 4,362,833 (Mune) / December 1982	1-112

^{*} Special categories of cited documents: ¹⁰"A" document defining the general state of the art which is not
considered to be of particular relevance"E" earlier document but published on or after the international
filing date"L" document which may throw doubts on priority claim(s) or
which is cited to establish the publication date of another
citation or other special reason (as specified)"O" document referring to an oral disclosure, use, exhibition or
other means"P" document published prior to the international filing date but
later than the priority date claimed"T" later document published after the international filing date
or priority date and not in conflict with the application but
cited to understand the principle or theory underlying the
invention"X" document of particular relevance; the claimed invention
cannot be considered novel or cannot be considered to
involve an inventive step"Y" document of particular relevance; the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such docu-
ments, such combination being obvious to a person skilled
in the art.

"Δ" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

06 September 1989

International Searching Authority

USA/US

Date of Mailing of this International Search Report

26 SEP 1989

Signature of Authorized Officer

Amy Hulina
Amy Hulina